



# **The Development and Commercialization of Biodegradable Selectively Branched Detergent Alcohols**

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# Surfactants

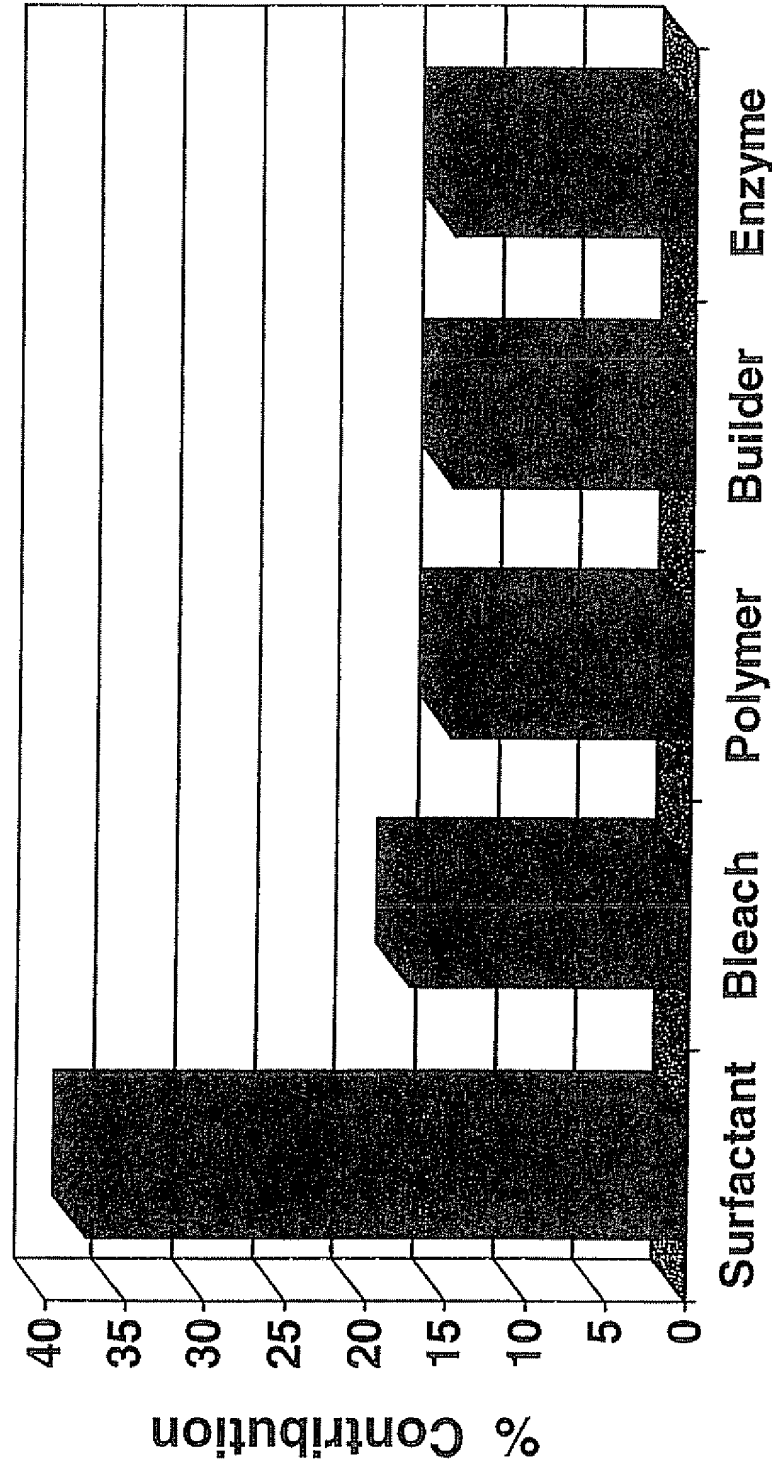
Multi-million ton/ year global business

Anionic surfactants are the largest group

They wet fabrics and soils; remove dirt and stains

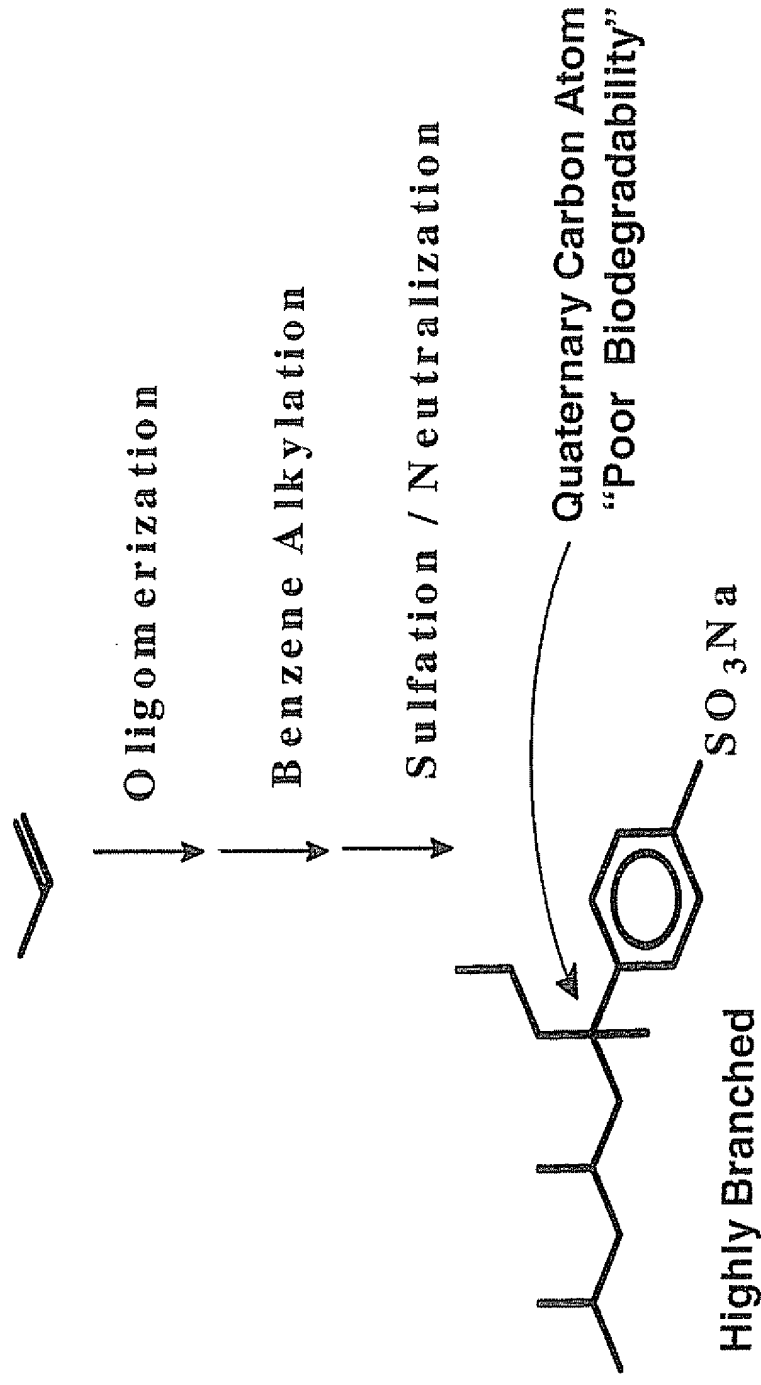
The single most important cleaning ingredient in most laundry and household cleaning products

# Performance Contribution to Detergency



\* G. Baillely et al., *Proceedings of the 5th World Conference on Detergents*, (2003)

# 1950's Vintage Alkylbenzene Sulfonate



## Surfactant Events – A Need for Innovation

1950's - Highly Branched Alkylbenzene Sulfonates, (ABS)  
slow biodegradation, foaming, aquatic toxicity?

1960's – ABS Regulation begins – Rapid replacement by  
Biodegradable Linear Alkylbenzene Sulfonates,  
Linear Alcohol Sulfates and Linear AES

**A Paradigm is born: “Alkyl branching is Bad”**

1970's - Movement to lower wash temperatures creates a  
need for better cold water detergency

1980's *The Alkyl Branching Paradigm is Challenged*

2000's - High Solubility Biodegradable, Selectively  
Branched Detergents are commercialized

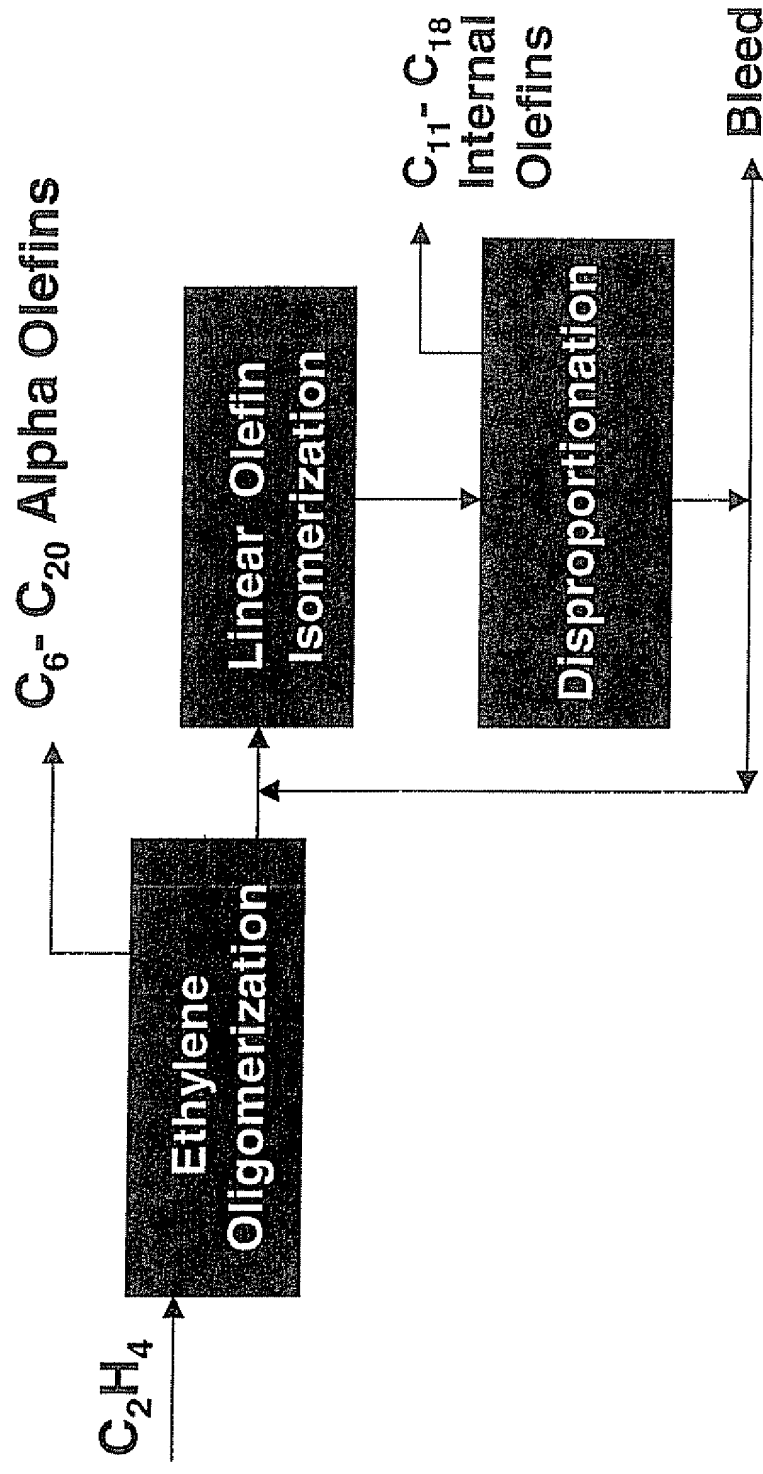
# Recent Trends in Washing Processes

- Lower Wash Water Temperature
- Lower Energy Consumption
- Shorter Wash Times
- Reduced Water Usage

# Desired Surfactant Properties

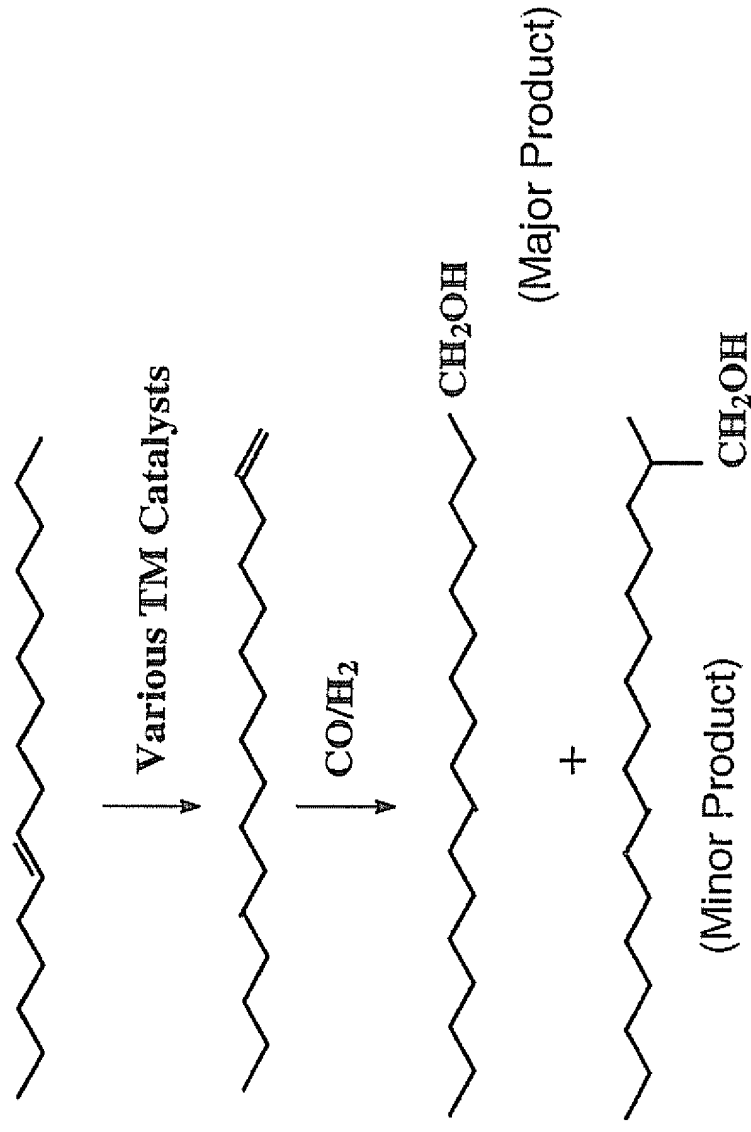
- Excellent Surface Activity
- Readily Biodegradable
- Superior Cold Water Detergency
- Improved Hard Water Solubility
- Ability to use Less Surfactant
- Affordable and Consistent Production

# Shell Higher Olefins Process (SHOP)



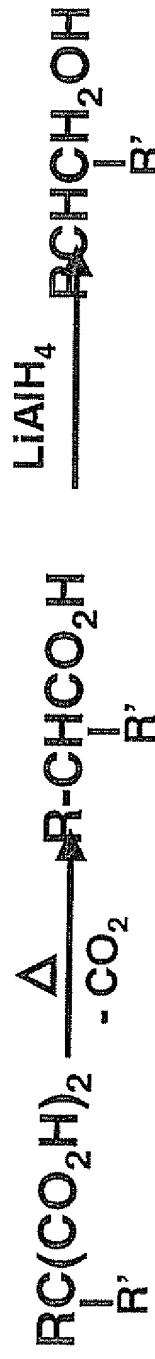
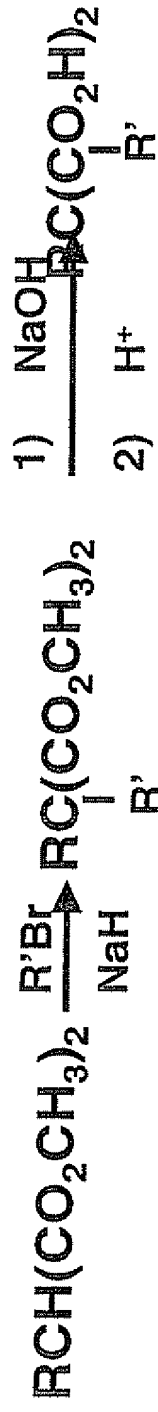


# Shell Hydroformylation Process (SHF)



# Model Compound Studies

## Malonic Ester Synthesis of 2-Alkyl Branched Alcohols

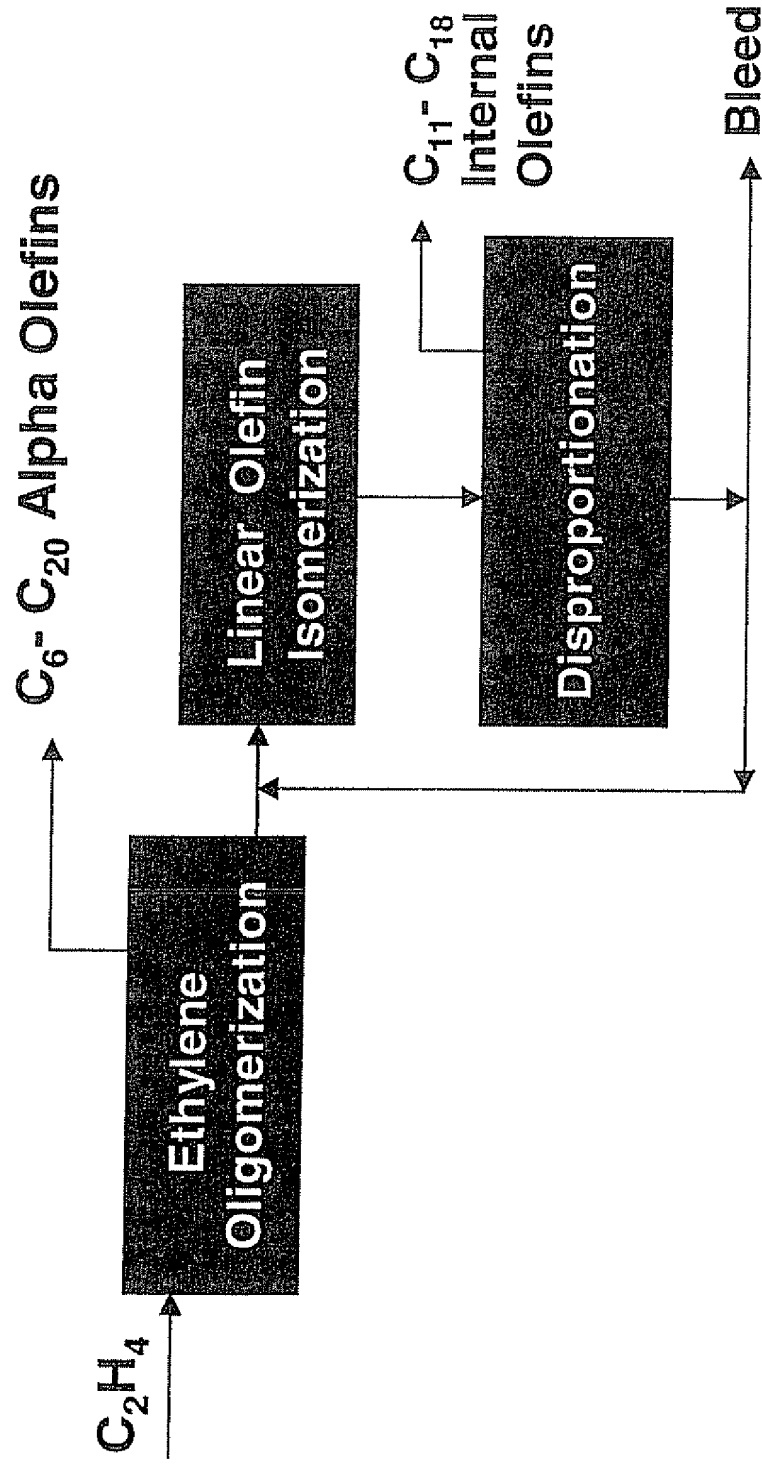


Alcohols were converted to the alcohol sulfate sodium salts by treatment with  $ClSO_3H$ , followed by neutralization with  $NaOH$

# How to Introduce Controlled Branching

- **Controlled Dimerization / Oligomerization of Lower Olefins**
- **Cross Metathesis Schemes**
- **Selective Skeletal Isomerization of Linear Olefins**
  - Use a proprietary, “pore engineered” zeolite catalyst
  - Makes mainly mono-branched olefins with the alkyl groups distributed at beneficial positions along the backbone
  - Very low level of quaternary carbon atoms in product

# Shell Higher Olefins Process (SHOP)

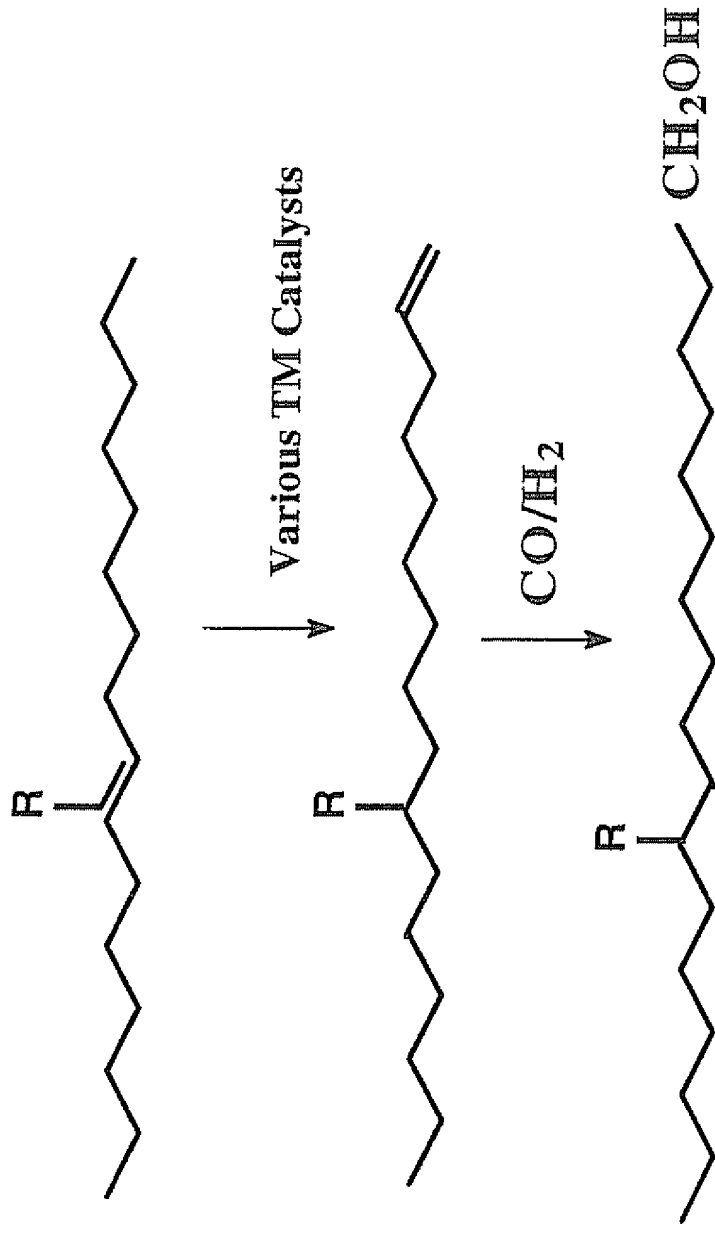


# Skeletal Olefin Isomerization Process

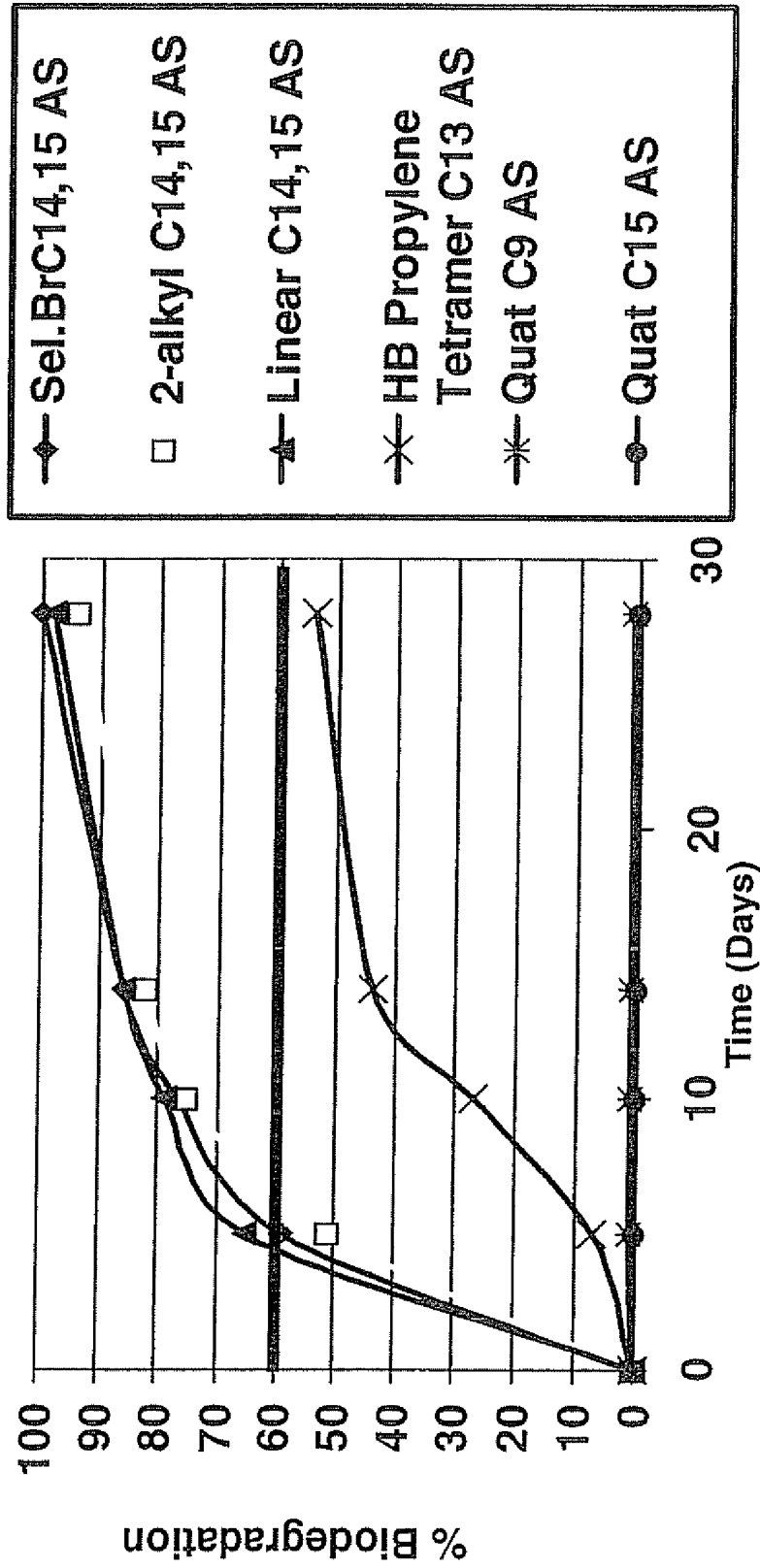
- Uses Alpha or Internal Olefins as Feedstocks
- Low Severity Operation
- Thermodynamic Equilibrium Conversion (>95%)
- Very High Selectivity (>98%)
- Multiply Regenerable Zeolite Catalyst
- Fully Compatible with the SHOP and SHF Processes
- Very High Catalyst Turnover Rate



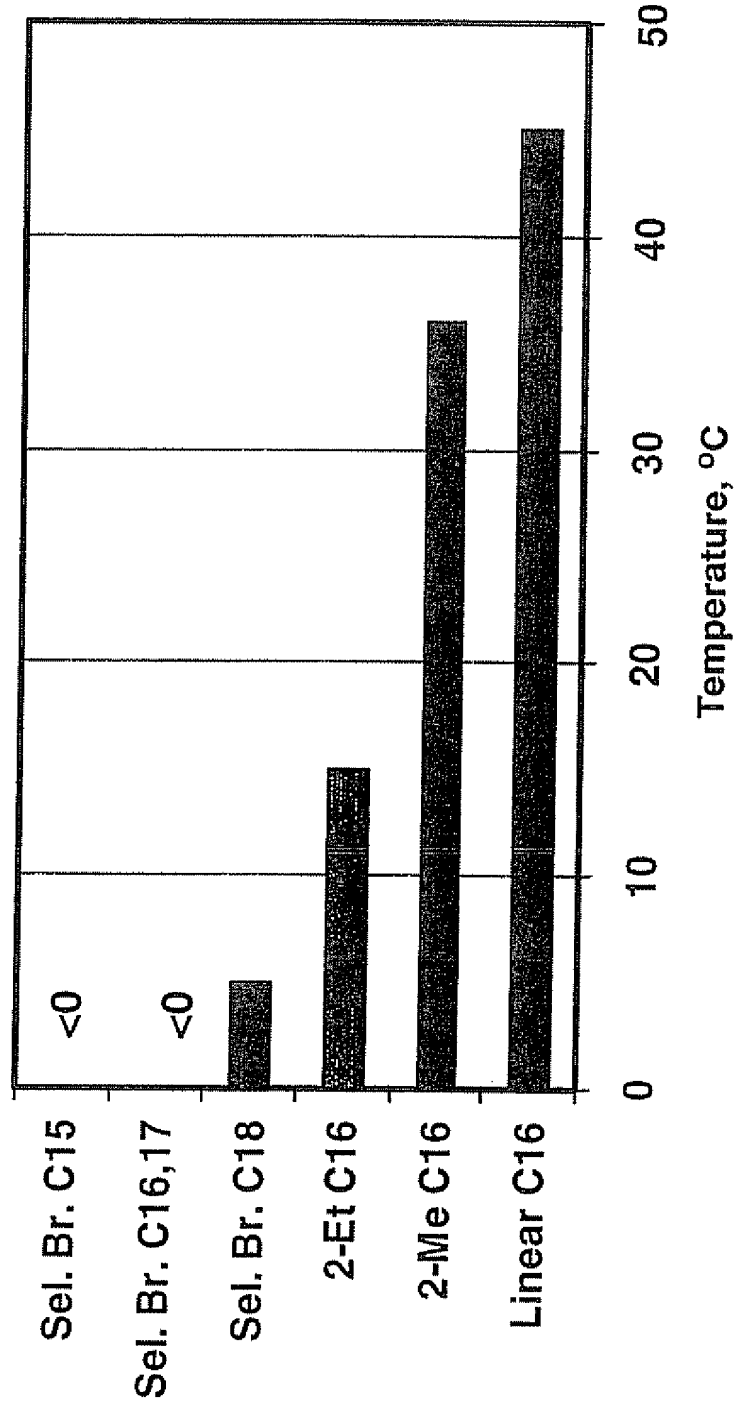
**R distributed at desirable positions along backbone**



# Closed Bottle Biodegradation Results for Various Alkyl Alcohol Sulfates

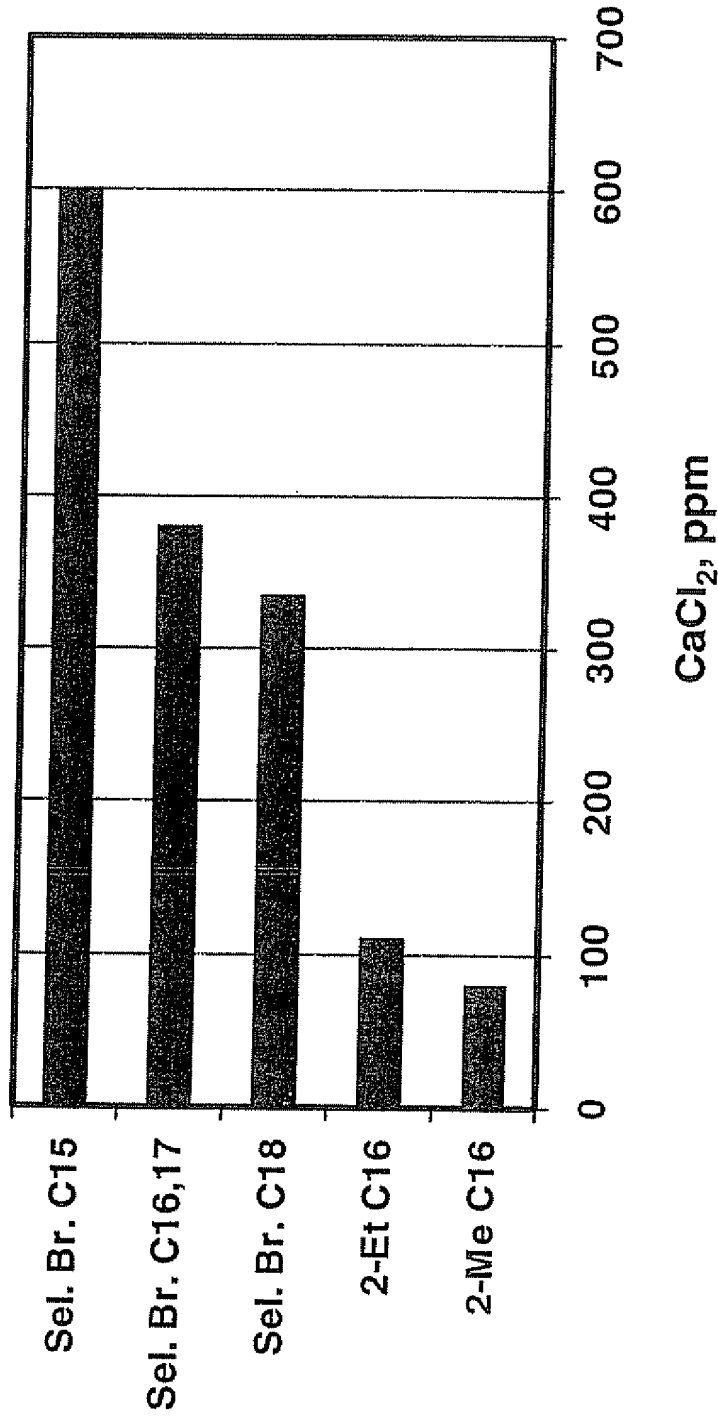


# Krafft Temperature of the new Selectively Branched Alcohol Sulfates

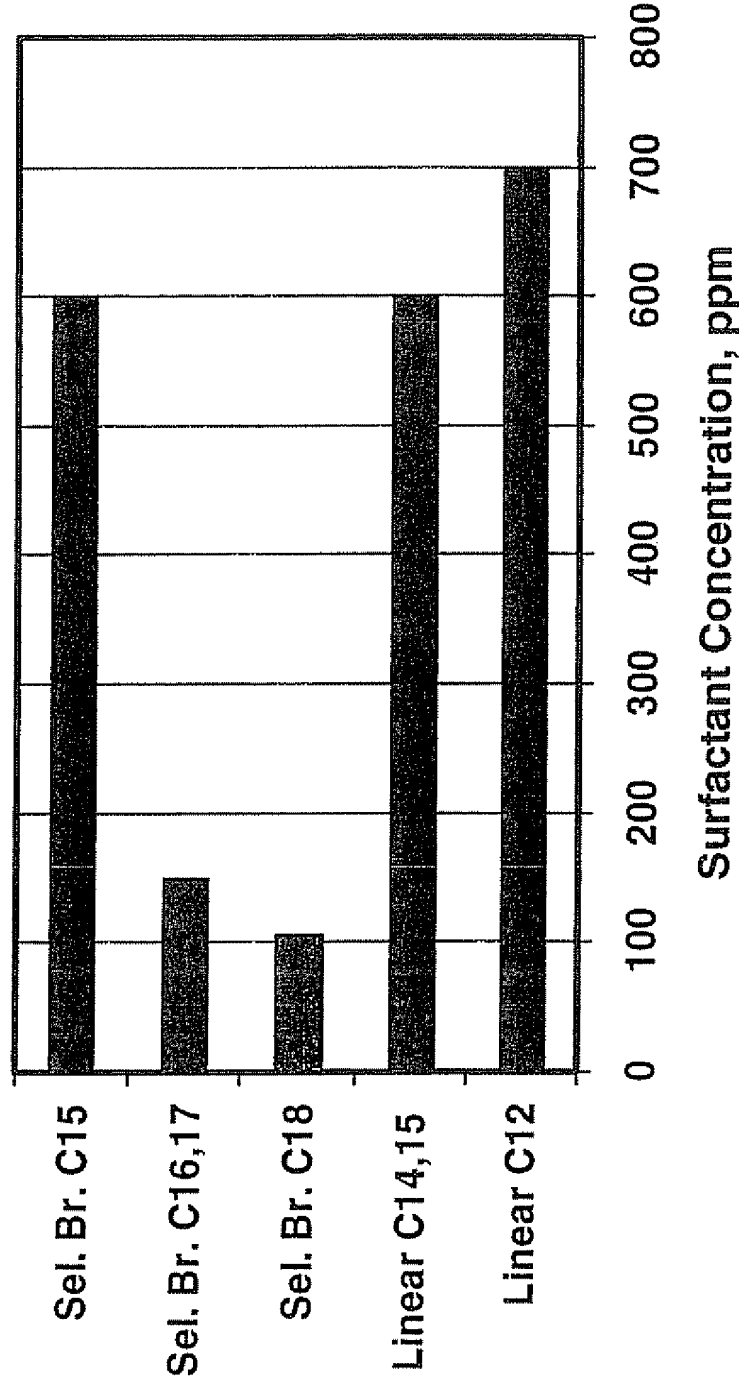




# Calcium Tolerance of the new Selectively Branched Alcohol Sulfates



# Critical Micelle Concentration of the Selectively Branched Alcohol Sulfates

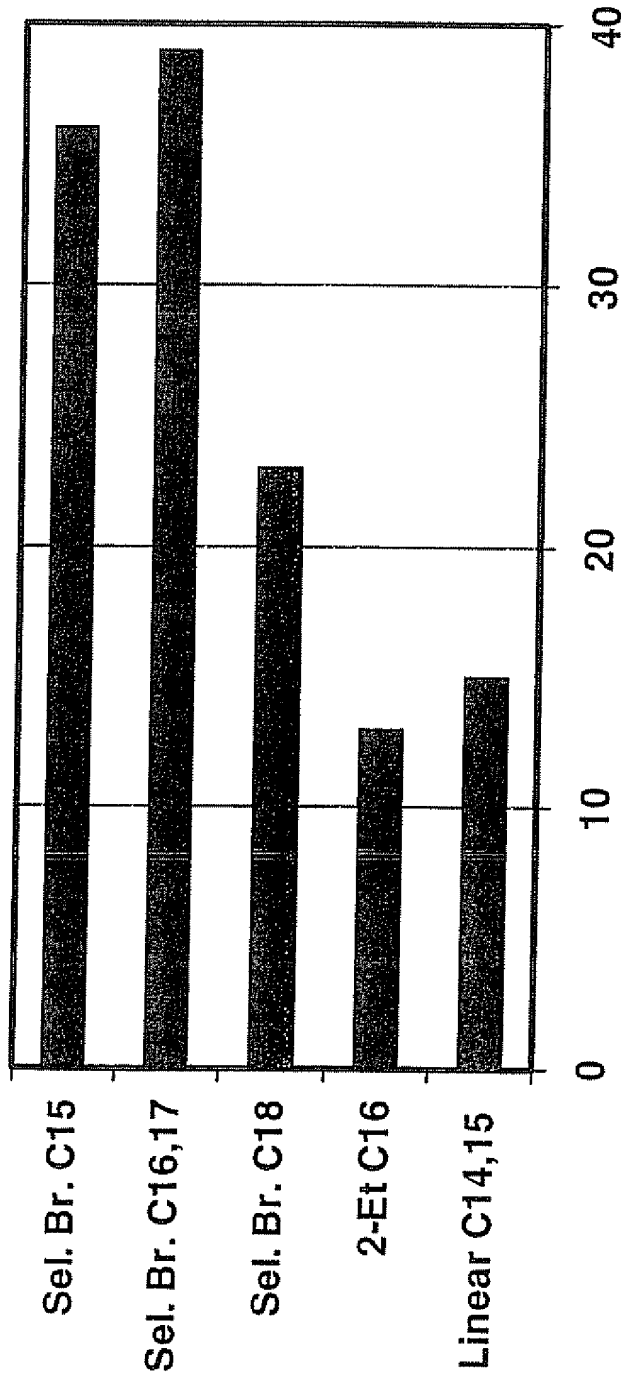




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# Detergency Performance of the new Selectively Branched Alcohol Sulfates

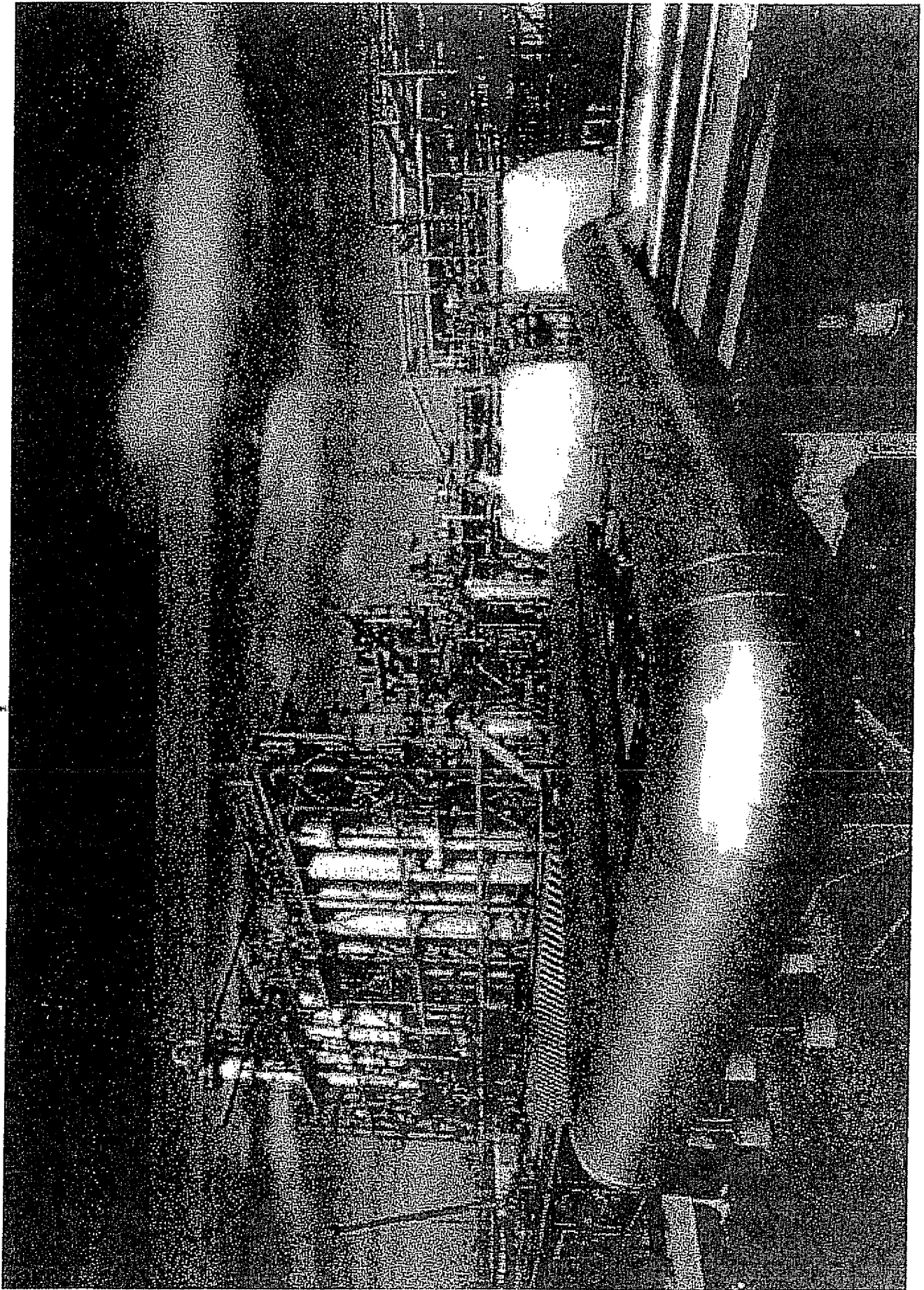
(at 10°C and 150 ppm Water Hardness)



% Soil Removal,  $LSD_{95} = 4$

## Partnering with Procter & Gamble

- P&G is a **Leading Global Supplier** to the Detergent Industry
- P&G conducted independent studies that pointed to a Primary Alcohol with a single methyl branch near the middle of the chain
- Evaluated various Shell “Selectively Branched” Alcohols
- Derivatized and formulated products based on the new alcohols
- A joint decision was made to commercialize the Innovation





# Commercialization

- Product was scaled up in several stages (6, 50 and 3700 tonnes)
  - Allowed Process Modeling and Design Optimization
  - Customer feedback
- P&G worked closely with Shell during the Process
  - HS&E Studies, Alcohol Conversion and Product Formulation
  - Logistics, Product Specifications
  - Market Development Work
- World-Scale Olefin/Alcohol Plant built at Geismar, LA. in 2001
  - On spec product produced within 12 hours of feed-in
  - Breakthrough Technology Confirmed in Operations
- Alcohols successfully formulated into Quick Dissolving Tide®

***“Tide is the most popular laundry detergent used in the USA”***



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## **New Opportunities**

### **▪ Personal Skin Care Products**

- Excellent Emollient / Moisturizer
- Non-oily
- Good Viscosity and Solubility Characteristics
- Biodegradable

### **▪ Industrial Fluids**

- Low Pour Point
- Good Stability

### **▪ Chemical Intermediates**

- Novel Composition
- Reagent for Various Industries



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## Acknowledgements

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